Yulong Liu, Zhaojia Dong, Youquan Guo and Ying Fu*

Crystal structure of 4,4'-(4,10-diphenyl-4,10-dihydropyreno[4,5-d:9,10-d']diimidazole-5,11-diyl)bis(*N,N*-diphenylaniline), C₆₆H₄₄N₆

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Abstract

C₆₆H₄₄N₆, triclinic, *P* $\bar{1}$ (no. 2), *a* = 9.773(2) Å, *b* = 14.406(3) Å, *c* = 18.385(4) Å, α = 72.64(3)°, β = 82.10(3)°, γ = 76.90(3)°, *V* = 2399.5(8) Å³, *Z* = 2, *R*_{gt}(*F*) = 0.0546, *wR*_{ref}(*F*²) = 0.1559, *T* = 153(2) K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of aniline (4.6 mL, 50.0 mmol), pyrene-4,5,9,10-tetraone (1.3 g, 5.0 mmol), corresponding aromatic aldehyde 4-(diphenylamino)benzaldehyde (3.3 g, 12.0 mmol), ammonium acetate (3.1 g, 40.0 mmol), and acetic acid (20 mL) was refluxed under nitrogen in an oil bath. After 2 h, the mixture was cooled and filtered. The solid product was washed with an acetic acid/water mixture (1:1, 150 mL). And then,

*Corresponding author: Ying Fu, College of Science, Northeast Agricultural University, Harbin, 150030, People's Republic of China, e-mail: fuying@neau.edu.cn

Yulong Liu and Zhaojia Dong: College of Science, Northeast Agricultural University, Harbin, 150030, People's Republic of China

Youquan Guo: Department of Basic, Heilongjiang Vocational College of Biology Science and Technology, Harbin, 150025, People's Republic of China

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.19 × 0.17 × 0.13 mm
Wavelength:	Mo <i>K</i> α radiation (0.71073 Å)
μ:	0.08 mm ^{−1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, ω-scans
θ _{max} , completeness:	25°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	18890, 8388, 0.073
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 4143
<i>N</i> (<i>param</i>) _{refined} :	649
Programs:	CrystalClear [1], SHELX [2, 3]

the crude product was separated by chromatography using CH₂Cl₂ as eluent and further purified by sublimation under vacuum. The product was collected as a yellow solid in yield 48.2%.

Experimental details

The C—H atoms were then constrained to an ideal geometry, with C—H distances of 0.95 Å. The *U*_{iso} values of the hydrogen atoms were set to 1.2*U*_{eq}(C).

Discussion

Pyrene belongs to one of the polycyclic aromatic hydrocarbons (PAHs) which possesses large planar π-system, strong π-stacking interactions, high photoluminescence (PL) efficiency and exceptionally long fluorescence lifetimes [4]. Its unique properties have inspired researchers from many scientific areas, making pyrene the chromophore of choice in fundamental and applied photochemical research [4–8]. Fused imidazoles, such as benzimidazole and phenanthro[9,10-*d*]imidazole, has been shown to be good electron-transporting materials and luminescent materials for OLEDs [9–11]. In continuation of our studies on the development of PAHs and *N*-containing heterocyclic compounds, herein we report a pyrene-imidazole compound.

In the crystal structure, the pyrene ring and the imidazole ring are almost coplanar, while the triphenylamine moieties keep propeller-shaped. The crystal showed a centrosymmetric, coplanar configuration and a slip-stacked packing mode along the long molecular axis. While the dihedral angle

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
N1	−0.3835(2)	0.88995(19)	0.58798(16)	0.0384(7)
N2	0.0424(2)	0.69369(18)	0.35504(15)	0.0315(6)
N3	−0.0845(2)	0.57386(17)	0.38299(15)	0.0304(6)
N4	0.5826(2)	0.41811(17)	0.12294(15)	0.0299(6)
N5	0.4438(2)	0.30767(18)	0.14101(15)	0.0334(7)
N6	0.8930(3)	0.11087(19)	−0.08717(16)	0.0409(7)
C1	−0.6125(3)	0.8471(2)	0.5936(2)	0.0408(9)
H1	−0.5932	0.8429	0.5425	0.049*
C2	−0.7394(4)	0.8307(3)	0.6327(2)	0.0590(11)
H2	−0.8062	0.8132	0.6087	0.071*
C3	−0.7711(4)	0.8392(3)	0.7068(2)	0.0607(12)
H3	−0.8603	0.8306	0.7326	0.073*
C4	−0.6717(4)	0.8602(3)	0.7418(2)	0.0501(10)
H4	−0.6914	0.8648	0.7928	0.060*
C5	−0.5423(3)	0.8749(2)	0.7036(2)	0.0417(8)
H5	−0.4737	0.8885	0.7288	0.050*
C6	−0.5128(3)	0.8698(2)	0.62919(19)	0.0323(8)
C7	−0.3199(3)	0.9646(2)	0.59748(19)	0.0341(8)
C8	−0.4014(3)	1.0502(2)	0.61258(19)	0.0380(8)
H8	−0.5012	1.0588	0.6178	0.046*
C9	−0.3372(3)	1.1229(2)	0.6200(2)	0.0436(9)
H9	−0.3939	1.1809	0.6308	0.052*
C10	−0.1921(4)	1.1128(3)	0.6120(2)	0.0483(10)
H10	−0.1490	1.1635	0.6165	0.058*
C11	−0.1114(3)	1.0276(3)	0.5975(2)	0.0478(10)
H11	−0.0116	1.0195	0.5917	0.057*
C12	−0.1744(3)	0.9537(2)	0.5913(2)	0.0419(9)
H12	−0.1172	0.8947	0.5827	0.050*
C13	−0.3149(3)	0.8327(2)	0.53696(19)	0.0335(8)
C14	−0.2555(3)	0.8786(2)	0.46545(19)	0.0359(8)
H14	−0.2655	0.9487	0.4492	0.043*
C15	−0.1827(3)	0.8226(2)	0.41845(19)	0.0355(8)
H15	−0.1413	0.8547	0.3703	0.043*
C16	−0.1683(3)	0.7192(2)	0.44014(19)	0.0313(7)
C17	−0.2317(3)	0.6751(2)	0.51075(19)	0.0354(8)
H17	−0.2259	0.6053	0.5261	0.042*
C18	−0.3031(3)	0.7305(2)	0.55899(19)	0.0360(8)
H18	−0.3441	0.6986	0.6073	0.043*
C19	−0.0729(3)	0.6641(2)	0.39213(18)	0.0298(7)
C20	−0.1996(3)	0.5217(2)	0.41042(19)	0.0300(8)
C21	−0.1862(3)	0.4434(2)	0.4754(2)	0.0406(8)
H21	−0.1063	0.4278	0.5041	0.049*
C22	−0.2905(4)	0.3871(3)	0.4985(2)	0.0519(10)
H22	−0.2825	0.3333	0.5436	0.062*
C23	−0.4051(4)	0.4089(3)	0.4564(3)	0.0569(11)
H23	−0.4751	0.3692	0.4718	0.068*
C24	−0.4187(3)	0.4885(3)	0.3917(2)	0.0546(11)
H24	−0.4989	0.5041	0.3631	0.066*
C25	−0.3153(3)	0.5457(3)	0.3681(2)	0.0437(9)
H25	−0.3241	0.6005	0.3236	0.052*
C26	0.0331(3)	0.5460(2)	0.33697(18)	0.0289(7)
C27	0.1086(3)	0.6205(2)	0.32081(18)	0.0297(7)
C28	0.2402(3)	0.6182(2)	0.27494(18)	0.0297(7)
C29	0.3151(3)	0.6942(2)	0.25954(19)	0.0335(8)
H29	0.2803	0.7493	0.2798	0.040*
C30	0.4408(3)	0.6888(2)	0.21441(19)	0.0368(8)
H30	0.4911	0.7412	0.2033	0.044*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C31	0.4945(3)	0.6093(2)	0.18538(18)	0.0331(8)
H31	0.5816	0.6071	0.1552	0.040*
C32	0.4218(3)	0.5312(2)	0.19995(18)	0.0298(7)
C33	0.2900(3)	0.5356(2)	0.24494(18)	0.0276(7)
C34	0.4658(3)	0.4458(2)	0.16994(18)	0.0303(7)
C35	0.3846(3)	0.3765(2)	0.18045(18)	0.0295(7)
C36	0.2546(3)	0.3778(2)	0.22731(18)	0.0296(7)
C37	0.1776(3)	0.3022(2)	0.24174(19)	0.0367(8)
H37	0.2103	0.2485	0.2198	0.044*
C38	0.0539(3)	0.3065(2)	0.2882(2)	0.0407(9)
H38	0.0023	0.2549	0.2984	0.049*
C39	0.0041(3)	0.3841(2)	0.31987(19)	0.0372(8)
H39	−0.0815	0.3854	0.3514	0.045*
C40	0.0775(3)	0.4613(2)	0.30641(18)	0.0297(7)
C41	0.2072(3)	0.4587(2)	0.25987(18)	0.0282(7)
C42	0.5632(3)	0.3342(2)	0.10661(18)	0.0311(7)
C43	0.6985(3)	0.4692(2)	0.09590(19)	0.0305(8)
C44	0.7011(3)	0.5326(2)	0.0234(2)	0.0390(8)
H44	0.6321	0.5380	−0.0101	0.047*
C45	0.8057(3)	0.5889(3)	−0.0005(2)	0.0505(10)
H45	0.8083	0.6331	−0.0505	0.061*
C46	0.9058(4)	0.5803(3)	0.0485(3)	0.0542(11)
H46	0.9756	0.6202	0.0328	0.065*
C47	0.9048(3)	0.5140(3)	0.1205(2)	0.0471(10)
H47	0.9758	0.5067	0.1533	0.057*
C48	0.8002(3)	0.4581(2)	0.1448(2)	0.0398(8)
H48	0.7985	0.4129	0.1943	0.048*
C49	0.6560(3)	0.2814(2)	0.05629(19)	0.0314(8)
C50	0.8026(3)	0.2608(2)	0.05222(19)	0.0352(8)
H50	0.8497	0.2858	0.0820	0.042*
C51	0.8814(3)	0.2050(2)	0.00577(19)	0.0378(8)
H51	0.9814	0.1912	0.0046	0.045*
C52	0.8150(3)	0.1689(2)	−0.03919(19)	0.0356(8)
C53	0.6687(3)	0.1887(2)	−0.03536(19)	0.0386(8)
H53	0.6218	0.1643	−0.0656	0.046*
C54	0.5912(3)	0.2429(2)	0.0114(2)	0.0387(8)
H54	0.4913	0.2547	0.0134	0.046*
C55	1.0173(3)	0.1357(2)	−0.13101(19)	0.0374(8)
C56	1.0379(3)	0.2326(2)	−0.1547(2)	0.0434(9)
H56	0.9678	0.2836	−0.1413	0.052*
C57	1.1596(4)	0.2560(3)	−0.1978(2)	0.0534(10)
H57	1.1730	0.3226	−0.2129	0.064*
C58	1.2619(4)	0.1830(3)	−0.2188(2)	0.0645(12)
H58	1.3447	0.1990	−0.2490	0.077*
C59	1.2414(4)	0.0865(3)	−0.1951(2)	0.0624(12)
H59	1.3112	0.0359	−0.2092	0.075*
C60	1.1216(3)	0.0620(3)	−0.1513(2)	0.0491(10)
H60	1.1101	−0.0050	−0.1350	0.059*
C61	0.8316(3)	0.0361(2)	−0.1003(2)	0.0382(8)
C62	0.8267(4)	0.0293(3)	−0.1732(2)	0.0503(10)
H62	0.8658	0.0740	−0.2159	0.060*
C63	0.7649(4)	−0.0426(3)	−0.1843(2)	0.0591(11)
H63	0.7634	−0.0479	−0.2345	0.071*
C64	0.7056(4)	−0.1063(3)	−0.1231(2)	0.0603(12)
H64	0.6619	−0.1549	−0.1309	0.072*
C65	0.7102(4)	−0.0991(3)	−0.0502(2)	0.0552(11)
H65	0.6692	−0.1428	−0.0077	0.066*
C66	0.7737(3)	−0.0291(2)	−0.0386(2)	0.0448(9)
H66	0.7777	−0.0255	0.0118	0.054*

between the pyrene-imidazole and phenyl ring connected to imidazole was near to 90°, keeping a certain distance between the molecules. The molecules adopt a stacking mode similar to the J-type aggregation along the crystallographic *c* axis in each column with $\pi \cdots \pi$ interactions formed between adjacent molecules. And each molecule interacts with one neighboring molecule *via* another C—H $\cdots \pi$ interactions.

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